Paper spray and related ambient ionization mass spectrometry applications in food control

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Abstract

In the analysis of food, mass spectrometry (MS) is one of the most universal and widely applied techniques. Recently, the outburst of the invention of several ambient ionization (AI) sources has innovated the way to conduct routine MS analysis in various fields, including food analysis. Paper spray ionization (PSI) is a representative example of AI methods that have been successfully coupled with a contemporary mass spectrometer. Our current work aims to summarize typical applications of PSI and the pertinent AI methods in diverse areas of food control, along with a discussion on their advantages and inherent limitations. Lastly, the prospects of these AI techniques for food control are presented.

Keywords: *Paper spray ionization, ambient ionization, mass spectrometry, food control.*

1. INTRODUCTION

Food is a fundamental determinant of human health, and the food industry occupies a major portion of the economy of many countries. Despite the importance of food safety for public health and the economy, food fraud is becoming increasingly widespread across countries [1]. For example, a total of 413 food fraud reports were identified in the beef supply chain by the Rapid Alert System for Food and Feed and Horizon Scan from 1997-2017 [2]. According to the World Health Organization, foods polluted with harmful bacteria, viruses, parasites, or chemical substances cause more than 200 diseases including cancers [3]. Also, because of consuming contaminated foods, some 600 million people suffer from a disease and nearly a half-million people lose their lives every year. Thus, food safety has become one of the major issues of concern for both authorities and consumers.

Mass spectrometry (MS) is one of the most universal techniques utilized in food control, due to its advantages of high sensitivity, selectivity, and speed. Because MS can measure the masses of small molecules to very large proteins, it can simultaneously detect various food components including trace contaminants, allergens, and adulteration [4-5]. MS has long been coupled with liquid chromatography and gas chromatography through conventional ionization sources such as electron ionization (EI), electrospray ionization (ESI), and atmospheric pressure chemical ionization (APCI), etc. However, these techniques may not be suitable for direct and high-throughput analysis of food samples because they require extensive sample preparation and long analysis times [4].

From the early 2000s, numerous ambient ionization (AI) techniques that are feasible to analyze various physical states (solid, liquid, and gas) of the sample were invented [6]. The term

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AI-MS denotes the technique that allows no or minimized sample preparation and ionization of analytes from their native environment to be introduced into a mass spectrometer [4, 7, 8]. The advent of AI-MS has received significant attention from various fields. AI-MS has been increasingly applied in food science due to its merits of simplicity, low cost, high-throughput of analysis. There are several ways to categorize AI-MS. Based on the desorption mode, AI-MS can be classified into three main groups: liquid extraction, plasma desorption, and laser desorption. Besides, AI-MS using other desorption mechanisms such as thermal, vibrational, acoustic, or evaporative activation can be called alternative sources. Moreover, combinations of multiple techniques have been introduced as integrated sources [9]. The classification of the desorption methods in AI-MS was displayed in Figure 1.

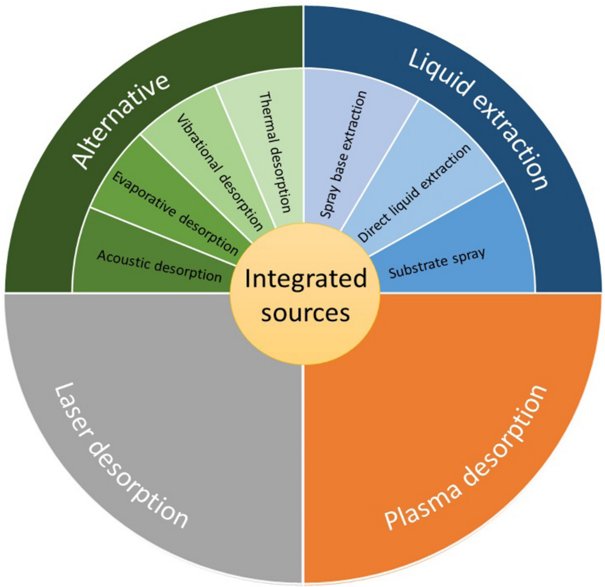

Figure 1. *Classification of desorption methods in AI-MS*

Paper spray ionization (PSI) is one of the most popular AI sources [8]. It is a typical successful instance of the substrate-based AI-MS, which belongs to the liquid extraction group in Figure 1. Compare to other methods in the same group, PSI has shown the greatest potential for quantitative analysis [9]. Since the invention of PSI by the Cooks group in 2010 [10], PSI has been applied widely in several fields of analytical chemistry such as clinical, food, forensic, environmental, mechanistic, and reaction monitoring studies [11].

In this review, we focus on the applications of PSI and the related AI methods on food analysis. First, the principles of PSI and the relevant AI techniques are introduced. Then, we summarize their recent developments and applications for different studies of food control. Next, the pros and cons of these ionization sources are discussed. Finally, the future potentials of PSI and the related AI sources are given.

2. PAPER SPRAY IONIZATION AND THE RELATED AMBIENT IONIZATION METHODS

PSI is a direct sampling and ionization method for MS analysis of complex matrix samples. In PSI, the sample is loaded onto a small triangular paper by directly dropping the sample solution on the paper or wiping the sample surface with the paper. A solvent is then added to wet the paper and extract the sample. Upon applying a high voltage to the paper, the sample is transported to the paper tip where ESI-like ionization occurs without pneumatic support [12]. The paper in a PSI source involves three analytical steps: sample collection, separation, and ionization [10]. The configuration of a PSI source is depicted in Figure 2.

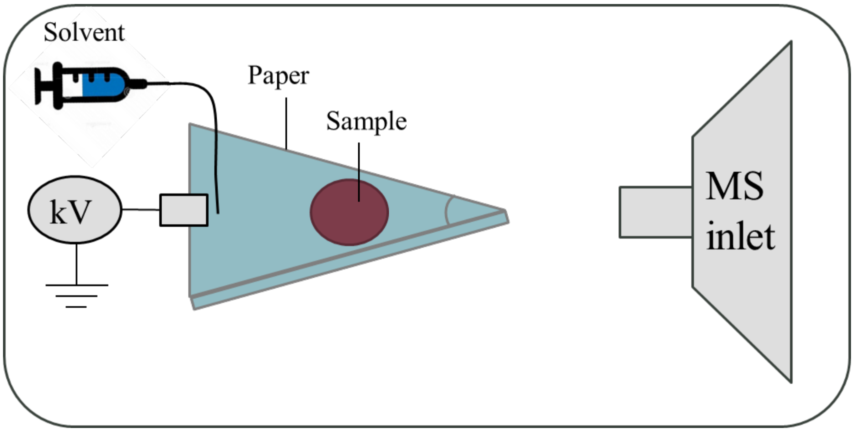

Figure 2. *Configuration of a PSI source*

Paper substrate has been widely used in sampling due to its distinctive properties. It is inexpensive, disposable, environmentally friendly, and easy to collect and store liquid samples in the dry form [13]. Although, in the original design, papers used in PSI were chromatography or filter papers made of cellulose fibers [10], multiple variations of PSI has been developed mainly by modifying the properties of the paper surface. Hydrophobic paper synthesized by exposure to a silanization reagent was proved to lower detection limits in the analysis of illicit drugs in biofluid and non-biological samples [14]. A urea-modified paper substrate demonstrated a much higher sensitivity compared to the intact paper in the negative ion mode by decreasing ionization competition [15]. Besides chemical modification, coating the paper with a specific material such as zirconia [16], polystyrene [17], silica [18], wax [19], and carbon nanotubes [20] was an alternative approach to obtain the desired properties of paper for better ionization. The use of paper with diverse properties made PSI feasible for various applications. Paper can also be folded into a cone shape to hold solid samples [21-22]. The PSI source consisted of a metal clip and a piece of paper as in Figure 2. Shortly after the invention, a disposable cartridge for PSI was designed and optimized for a fast clinical analysis [23]. Subsequently, 3D-printers were utilized to fabricate PSI sources with special features such as fast wetting and continuous solvent supply [24], microfluidic printed channel [25], and integration of an embedded electrostatic lens and a manifold for internal sheath gas distribution and delivery [26].

The mechanism of PSI in the positive ion mode was supposed to resemble nano-ESI, although PSI often utilizes a higher applied voltage because of the difference in capillary size [10]. From a PSI mechanism study, two spraying modes that occur sequentially were observed in a single PSI setup [27]. When the solvent was rich at the beginning of PSI, mode one featuring unstable multi-jet spray that dominantly generates proton-transfer ions in the mass spectra was shown. The multi-jet spraying was assumed to be a unique feature of PSI in comparison with conventional ESI. Mode 2 appeared when most of the solvent was almost depleted and thus smaller droplets were produced. In the second mode, the ion current increased sharply and some electron-transfer species such as radical cations or anions possibly generated by corona discharge were observed in the mass spectra. They supposed that the ionization mechanism was a field-enhanced electrospray. In another study on PSI at an extremely high voltage (around 6 kV), the mechanism of PSI was described to obey APCI when the spray solvent was nonpolar [28]. This new type of ionization method was named paper spray chemical ionization, which is beneficial for the analysis of low and nonpolar aromatic compounds. The Cooks group also introduced "zero voltage PSI," whose ionization mechanism is far different from that of the original PSI [29]. In this circumstance, PSI occurs by the pneumatic force of a high vacuum of the mass spectrometer instead of the electric force.

Since the birth of PSI, several AI sources based on substrates alternative to paper have been developed. The Yao group invented wooden tip ESI-MS (WT-ESI-MS) that employs a wooden toothpick for sampling and spraying of analytes [30-31]. They also developed an automated WT-ESI-MS, which achieved an analysis speed of around 15 seconds per sample [32]. The porous toothpick can carry a liquid sample, and its cellulosic surface similar to paper allows chemical modifications targeting hydroxyl groups [30-33]. Thread spray AI was another cellulose-based substrate spray technique that was developed to detect various capsaicinoids from pepper fruits [34]. Direct analysis of plant compounds was conducted simply by the leaf spray method [35]. This technique can also apply to other parts of a plant, such as a root, stem, flower, fruit, and seed. Demian and coworkers reported an AI method using coffee bean slice as a substrate to detect endogenous compounds [36]. Besides the cellulose-based substrates mentioned above, polymers, membranes, glass, needles, coated blades were noncellulose-based substrates that have been alternatively utilized for AI [13]. For a precise quantitative analysis of herbal powders, pipette-tip ESI-MS that uses an ion source combining a pipette tip with a syringe pump was also introduced [37].

3. APPLICATIONS OF PSI AND RELATED AI METHODS IN FOOD CONTROL

The analytical methods in the field of food safety need to be fast and cost-effective while providing the necessary accuracy. PSI has the characteristics to meet these requirements and becomes one of the most popular AI sources in food control. In this section, we summarize the applications of PSI and the related AI sources for different purposes of food safety covering detection, monitoring, characterization, classification, and authentication of regulated compounds.

3.1. Detection of regulated compounds

Agrichemical residues in food have always been one of the prior issues in food safety. In the first introduction of PSI, the Ouyang group illustrated the analysis of agrochemicals (thiabendazole) on lemon peels [12]. PSI was also applied to screening pesticides in fruits and vegetables with two sampling methods: wiping the sample surface with paper and applying a homogenized sample directly onto paper [38]. With both of these sampling approaches, PSI achieved the limit of detection below maximum residue levels. Subsequent researches demonstrated that PSI–MS could be used as an alternative technique to conventional chromatography-MS for monitoring pesticide concentrations in tomatoes during the pre-harvest interval [39], detecting multiple pesticides in wine [40], and measuring herbicides in crop extracts [41]. Agrochemical analysis in vegetables can be performed directly by leaf spray MS without the extraction step unlike PSI [42]. For animal origin food samples, PSI succeeded in screening multi-class antimicrobial residues [43]. Complex matrices such as milk or honey contain a high concentration of sugar, protein, lipid, and others that often causes ionization suppression. A molecularly imprinted polymer-coated wooden tip was generated to analyze trace antibiotics that accomplish a more sensitive analysis of complex samples [44]. Similarly, a molecularly imprinted polymer membrane spray ionization method provided satisfactory performance for quantitative analysis of some herbicides in fruits [45].

In 2012, the Cooks group reported the success of a silica-coated PSI method in the determination of some food contaminations: clenbuterol, terbutaline, salbutamol, ractopamine, and melamine in pork and beef, sudan red in chili powder, and bis(2-ethylhexyl) phthalate, and bis(2-ethylhexyl) adipate in sports juice [46]. With one step of dilution, 4-methylimidazole (4-MEI) in caramel and beverage can be rapidly detected by applying the sample to unmodified chromatography paper. The detection limit in each matrix was much lower than the level of 4-MEI in tested cola beverages, caramel food colors, and the debated levels of risk [47]. Recently, Meng and coworkers have coupled a syringe spray ionization with a miniature mass spectrometer, which successfully demonstrated its applicability to on-site identification of various compounds including sildenafil, vardenafil, sudan red, rhodamine B, and forchlorfenuron in different types of foodstuff [48]. Contaminations contained not only in foodstuff but also in food packing materials are regulated. Bisphenol A and its analogs in food packaging products can be detected by PSI or direct sample spray after a simple treatment with dichloromethane [49].

The detection of health-beneficial components in food products also requires a high-throughput analytical method to save time and cost. PSI was also utilized to evaluate the total phenolic compounds and antioxidant activity in detox mixed beverages [50], anti-inflammatory molecules in olive oil [51], resveratrol in red wines [52], and benzoic acid and vitamin C in beverages [53].

3.2. Monitoring and characterization

With their advantages of speed and sensitivity, PSI and the related AI sources are ideal tools for monitoring and characterizing food constituents. Some physicochemical properties of food can be varied during the production, storage, and processing of food. Pesticides are utilized in different stages of the cultivation of fruits and vegetables. However, farmers may crop them earlier than the due harvest time and store them at low temperatures. Moura *et al.* monitored the pesticide concentrations during the pre-harvest intervals by PSI-MS [39]. Several scientists used leaf spray MS for *in vivo* analysis of plants and characterization of plant materials [35, 54]. Other parts of the plant can also be employed for AI similarly to leaf. Compare to PSI-MS, these techniques by pass the sample treatment as the sample itself is used as a substrate for direct spray [42].

3.3. Classification and authentication

Food fraud that threatens both reputation of food producers, as well as the health of consumers, is a growing issue in food safety. PSI-MS has proved its potential in the area of food classification and authentication. Coffee is an example of agricultural products that are frequently counterfeited. It is an important commodity for many countries and the quality is critically affected by its geographic origin. In line with this, Garrett *et al.* explored the application of PSI-MS combined with multivariate statistical tools (principal component analysis and hierarchical cluster analysis) to discriminate green arabica coffee beans by their different regions in the country [36]. Similarly, PSI-MS profiling was exploited as a marker for the classification of essential oils in beverages and flavored foodstuff [55], and for distinguishing among authentic and counterfeit samples of blended Scottish whisky [56].

4. CHALLENGES AND OPPORTUNITIES

Like other new analytical methods, PSI and the related AI sources are still in the stage of development, so they need to overcome some technical issues to become a confirmation method in food analysis. This situation opens a challenge but also provides an opportunity for food scientists. Despite many advantages of PSI and the related AI techniques, low reproducibility is one of their inherent limitations. The mass spectra obtained by these ionization methods in replicate measurements typically suffer from high fluctuations of the absolute signal intensities, which can be influenced by the sampling process, surrounding environments, ionization efficiency, and various ion source parameters [8]. The low reproducibility issue can be alleviated by using an internal standard and well-optimized ionization source parameters. The development of PSI cartridge [24, 26] was spurred by an effort to stabilize the PSI signals from one measurement to another. Besides, Ouyang and his colleagues devised a moving stage assisting the traditional PSI source, which allowed the analysis of therapeutic drugs in blood and drug compounds in beef up to seven seconds per sample [57]. In the same context, Zhu and Huang integrated a two-dimensional rotating platform with the assembly of an induced high voltage into the PSI source [58]. A relatively rapid analytical speed of 2.6 seconds per sample was achieved and the relative standard deviation was 10.0% for ten repeated measurements of amitriptyline via this device.

Because sample preparation and sample separation by chromatography are minimized or eliminated, ion suppression due to complex matrices often occurs in AI-MS. To address this issue, many studies reported modified papers or new substrates for direct spray ionization (as described in the second section). There have been great efforts for modifying the sprayed substrate in order to reduce the interference and enhance the selectivity in the ionization of analytes. For instance, carbon nanotube-modified PSI-MS was utilized in direct extraction, desorption, and ionization of in-gel intact proteins [20]. In the optimized condition, the authors successfully separated a mixture of cytochrome c, lysozyme, and myoglobin by native electrophoresis and subsequently analyzed them with a detection limit of 10 ng per band with their developed method. Another example of an improved analysis by the use of a modified substrate was a 2D wax printed PSI source that provided high sensitivity (sub ng/mL levels) and good quantification precision (<10% RSD) [19]. Compared with un-waxed papers, stable electrospray with better linearity and precision can be generated with the 2D wax printed ion source by focusing the spray solvent on the designed area.

5. FUTURE PROSPECTS OF PSI AND RELATED AI METHODS IN FOOD CONTROL

PSI and the relevant AI sources are well-known for their features of simple and fast analysis. AI sources including PSI can be coupled with a miniature mass spectrometer facilitating on-site analysis of analytes in food. Recently, a group of scientists in China reported the methodologies that combine AI with a miniature ion trap mass spectrometer and applied these configurations to an on-site screening of food adulterants by taking advantage of the simplicity and versatility of sample preparation and high sensitivity [48]. Therefore, the production of commercial PSI or other AI cartridges for portable MS would have great potential in the field of food control.

The applications of AI-MS, as well as PSI and the related AI methods, can be leveled up with the advancement of their supporting techniques. As mentioned in section 3, statistical tools were used to solve the complexity of PSI-MS spectra in the characterization and detection of food adulteration. It is full of promise that artificial intelligence can assist the application of AI-MS in complex food matrices. Moreover, it is necessary to develop user-friendly software specific for PSI and other AI methods, because most of the studies based on AI-MS rely on the software designed for conventional chromatography MS.

6. CONCLUSIONS

This review describes the principle and technical progress of PSI and related AI methods since their invention. The advantages of these AI sources are illustrated by several publications in various analysis areas including food control. A summary of the applications of PSI and the pertinent AI tools in different purposes of food analysis including detection of regulated compounds in food, monitoring, and characterization of food constituents, and classification and authentication of food contents are given along with their future perspective. We expect that PSI and the related AI methods along with the progress in portable mass spectrometer instrumentation and the supporting software would make a big contribution to a routine analysis in food control laboratories in the future.

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Ứng dụng khối phổ ion hóa sử dụng giấy và ion hóa trực tiếp chất nền trong kiểm soát thực phẩm

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Tóm tắt

Trong phân tích thực phẩm, khối phổ là kỹ thuật được sử dụng ngày càng rộng rãi. Những năm gần đây thế giới chứng kiến sự ra đời của nhiều loại nguồn ion hóa mới ghép nối với khối phổ, chúng đã thay đổi cách mà các nhà khoa học phân tích thực phẩm. Nguồn ion hóa sử dụng vật liệu giấy để ion hóa mẫu và các biến thể tương tự khác của nó là những ví dụng thành công của nhóm các nguồn ion hóa mới này. Trong bài tổng quan này, những ứng dụng của nguồn ion hóa sử dụng giấy và các biến thể của nó trong việc kiểm soát thực phẩm với những mục đích khác nhau đã được trình bày. Những hạn chế vốn có và phương pháp khắc phục của kỹ thuật này cũng được bàn luận trong bài viết này. Ở phần cuối cùng, chúng tôi sẽ đưa ra những ý kiến về tiềm năng phát triển của các nguồn ion hóa mới này trong tương lai.

Từ khóa: *Ion hóa phun trên giấy, ion hóa trực tiếp, khối phổ, kiểm soát thực phẩm.*

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